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# Hydrothermal synthesis of Ag modified ZnO nanorods and their enhanced ethanol-sensing properties

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ABSTRACT

Silver (Ag) nanoparticles decorated zinc oxide (ZnO) nanorods were synthesized by a simple hydrothermal treatment for enhancing gas-sensing performance toward ethanol. The X-ray diffraction (XRD) and energy dispersive X-ray spectroscopic (EDS) results indicate the presence of Ag nanoparticles. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results reveal that Ag nanoparticles are tightly anchored on the surface of ZnO nanorods. The UV–vis diffuse reflectance spectroscopy (UV–vis DRS) results confirm that the band gap energy is decreased due to the decoration of Ag. The gas sensing performance of as-synthesized materials was investigated at different working temperatures and toward various ethanol concentrations. The gas-sensing results exhibit that the 1 wt% Ag/ZnO sensor shows the highest sensitivity of 389.6 toward 800 ppm ethanol and fast response among all the sensors. The improved response of Ag/ZnO sensors is ascribed to the catalysis and spillover effect of Ag. This result makes Ag/ZnO sensor a very promising gas sensing material for gas detection.

## 1. Introduction

Gas sensors have attracted much attention for detecting explosive and toxic gases in our environment. Metal oxide semiconductors having irreplaceable advantages of low cost, small size, high sensitivity and facile integration are widely used for detection of gases [1,2]. Amongst the large number of metal oxides, zinc oxide (ZnO), an n-type semiconductor oxide, has been reported as a preferable candidate for gas sensing applications due to its wide band gap (3.37 eV), high electron mobility, ideal chemical and thermal stability [3–6]. However, the further applications of metal oxide based sensors are limited by the high working temperature, low sensitivity and poor selectivity. In order to overcome these existing shortages and to improve sensing characteristics, further work should be performed [7,8]. ZnO nanostructures have been prepared at different morphologies, such as nanosheets, nanoflowers, microwires, nanotubes and nanocones. Similar to the sensing behavior of other metal oxides, different nanostructures exhibit diverse sensing characteristics [9,10]. In view of relatively low response and poor selectivity of pure ZnO based gas sensor, there exists urgent need to improve its sensing characteristics [11]. Hence, some studies have been reported on the improvement of gas sensing performance of ZnO. For example, Drobek [12] et al. reported the preparation of ZIF-8 molecular sieve membrane encapsulated ZnO nanowire (ZnO@ZIF-8 NWs), which shows the better selectivity at 300 °C for $H_2$ than ZnO nanowires sensor. Viter [13] et al. reported the fabrication 1D ZnO/polyacrylonitrile (PAN) nanostructures by the combination of electrospinning and atomic layer deposition (ALD) for optical sensor detection. Recently, the addition of noble metal to semiconducting oxide has been applied as a significant and effective technique for the enhancement of gas sensing performance [1,14].

It has been reported that the introduction of noble metal particles on metal oxide surface is identified as an efficient strategy to enhance gas sensitivity, which can influence the material's electronic and chemical distribution beneficial to the adsorption of oxygen species [15]. Ag nanoparticles have been reported to be a helpful catalyst to accelerate the reaction between oxygen species and target gas and greatly enhance their gas-sensing properties [16]. Meng et al. synthesized Ag-decorated ZnO nanosheets via a solvent reduction method, and the as-prepared products show a higher sensitivity toward ethanol with a detection limit of 1 ppb [17]. Cui et al. prepared Ag-ZnO nanorods through a two-step process and the Ag-ZnO sensors show dramatically high response to HCHO in UV light photoelectric at RT [18]. Chen et al. prepared Ag-doped ZnO nanostructures by the hydrothermal process, and the 1 wt% Ag-doped ZnO nanostructures based sensor displays better gas-sensing

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property to 10 ppm ethanol at 260 °C [19]. Nonetheless, it is difficult to control the size and distribution of Ag particles on the surface of ZnO nanostructures. Thus, it is still necessary for researchers to find an effective method to synthesize ZnO/Ag composite with high sensitivity.

Herein, we synthesized pure and Ag nanoparticles decorated ZnO nanorods by the facile hydrothermal route, and fabricated an ethanol sensor by coating the sensing material onto the ceramic substrate. The gas-sensing properties of all products to ethanol were investigated at different temperatures. As a result, the sensing response is improved markedly by the decoration of Ag on ZnO nanorods. Especially, the sensor of 1 wt% Ag nanoparticles decorated ZnO nanostructures exhibits a high sensitivity and selectivity toward ethanol. Finally, the enhanced gas sensing mechanism of Ag/ZnO nanorods was discussed.

## 2. Experimental

### 2.1. Materials

All chemicals were the analytical-grade reagents and used without further treatment. Zinc nitrate, silver nitrate and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (China), distilled water was made in our laboratory.

### 2.2. Synthesis of ZnO and Ag decorated ZnO (Ag/ZnO) nanorods

The samples were prepared through the hydrothermal route, and the synthesis illustration of Ag/ZnO nanorods is displayed in Fig. 1. The preparation process is briefly described as follows: The $Zn(NO_3)_2{\cdot}6H_2O$ (4.16 g) was dissolved into 320 mL of DI water with stirring for 30 min. Subsequently, 40 mL of NaOH solution (4 mol/L) and certain amount of $AgNO_3$ (0 wt%, 0.5 wt%, 1.0 wt% and 2.0 wt%) was added into the above mixture solution under continuous stirring for 10 min to obtain the reaction solution system. The uniform solution was transferred into the Teflon-lined autoclave and heated at 180 °C for 12 h under autogenous pressure. Then, the final product was centrifuged and washed with deionized water for several times, and dried in oven at 65 °C. At last, the prepared samples were calcined at 400 °C for 2 h in the muffle furnace.

### 2.3. Characterizations of the samples

The crystalline phase structure of the as-synthesized products was characterized via XRD using a Bruker-AXS diffractometer (D8 advance) with Cu *Kα* radiation. The morphologies of samples were investigated using FESEM (Quanta 250 FEG) and TEM (JEOL JEM-2100). Elemental composition of powders was studied by EDS that was connect to FESEM (Quanta 250 FEG). UV–Vis diffuse reflectance spectra (UV–Vis DRS) was performed for products by a UV–Vis spectrometer (Beijing Puxi GI Co., Ltd, TU-1900).

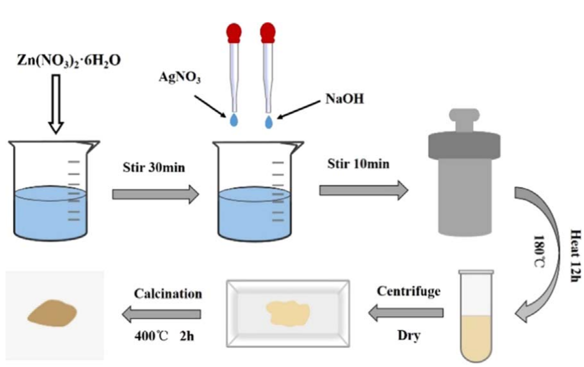


**Fig. 1.** The synthesis illustration of Ag/ZnO nanorods.

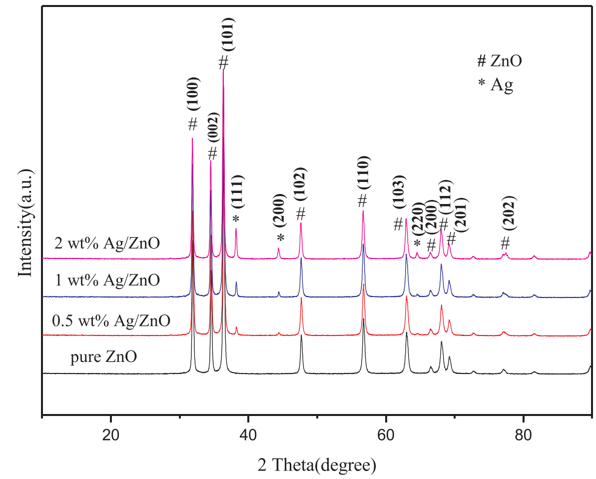


**Fig. 2.** The XRD patterns of pure ZnO and Ag/ZnO nanorods.

### 2.4. Measurement of gas sensing performance

The gas sensing properties of ZnO and Ag decorated Ag/ZnO nanorods were investigated by the sensor measuring system of CGS-4TPS (Beijing Eklite Tech Co., Ltd, China). For fabricating sensors, the synthesized products were mixed with ethanol to prepare a paste that painted onto the ceramic substrate (7 mm width, 13.4 mm length). After aged at 60 °C for 8 h, the fabricated sensors were fixed on the temperature controller plate. In the process of measurement, the fabricated sensors were adjusted to a suitable temperature by the temperature controller. After the resistances of sensors reach a stable state, a certain amount of ethanol was injected into test chamber to get the response curve. After the response reaches a steady value, the ceramic substrate was in air again by releasing the test gas. The gas response is estimated as *Ra/Rg* ratio, where *Ra* is the electrical resistance in air and *Rg* is the electrical resistance in test gas, respectively.

## 3. Results and discussions

### 3.1. Crystal structure and morphology

Fig. 2 shows the XRD patterns of ZnO and Ag/ZnO nanorods. The diffraction peaks at 31.92°, 34.58°, 36.42°, 47.71°, 56.74°, 63.02°, 68.08°, and 69.24° can be unambiguously indexed to (100), (002), (101), (102), (110), (103), (112) and (201) planes of ZnO with hexagonal phase (JCPDS Card No.36-1451), respectively. The sharp diffraction peaks indicate that the ZnO materials are highly crystalline. As expected, the Ag/ZnO nanorods show obvious characteristic diffraction peaks at 38.20° 44.38° and 64.54° which can be corresponding to (111), (200) and (220) planes of cubic phase Ag (JCPDS Card No.04-0783), respectively. The Ag peak intensity becomes stronger with the increase of Ag concentration, which indicates the presence of Ag in obtained composites.

The morphological investigation of resulting samples was performed by SEM, TEM and HRTEM. Fig. 3(a) reveals that pure ZnO has a radial structure assembled with nanorods. The average width and length of the ZnO nanorods is 200 and 900 nm, respectively. Fig. 3(b) shows the SEM images of Ag/ZnO nanorods. We can see clearly that the Ag nanoparticles with diameters ranging from 50 to 100 nm are firmly deposited on the surface of ZnO nanorods, and these Ag particles have a slight agglomeration. Fig. 3(c) displays the EDS spectrum of Ag/ZnO nanorods, indicating the existence of Ag element. According to XRD and EDS analyses, it can be concluded that Ag exists as a pure metal phase in Ag/ZnO composite.

To further verify the above inference, the TEM analysis was performed. Fig. 4(a) further reveals the radial structure of pure ZnO